P. C. Tully

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INTERNAL REPORT

TESTS ON THE STATISTICAL METHOD OF TREATING THE 0° C HELIUM

DATA OBTAINED FROM A BURNETT COMPRESSIBILITY APPARATUS

BY

B. J. Dalton

BRANCH Fundamental Research

PROJECT NO. 4335

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TESTS ON THE STATISTICAL METHOD OF TREATING THE 0° C HELIUM DATA OBTAINED FROM A BURNETT COMPRESSIBILITY APPARATUS

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B. J. Dalton[1/]

ABSTRACT

This report describes tests on the statistical method of treating the 0° C helium data obtained from the Helium Research Center's Burnett compressibility apparatus. Tests have been carried out to show: 1. the effect an error in the determination of the pressure distortion corrections of the high-pressure bombs produces in the compressibility factor, Z, which is a function of virial coefficients, and in the value of the volume ratio at zero pressure, N; 2. the effect an error in the fractional change in the effective area of the piston (at 25° C, P=0) with pressure induces in Z and N; and 3. the effect an error of ignoring the change in volume of the containers with pressure produces in Z and N. The statistical tests are given for the compressibility factor isotherm expressed in terms of the Berlin expansion in powers of the pressure, assuming the contribution of fourth and higher virials to be negligible.

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Work on manuscript completed May 1966.

INTRODUCTION

Compressibility data obtained by the Burnett method involve: 1. calculating pressures from a series of experimental observations of gage temperatures, gage pressures, barometer readings, barometer temperatures, and relative humidity values; 2. determining corrections for the pressure distortion of the high-pressure containers; and 3. evaluating the parameters appearing in the expression for the compressibility of the gas and also to evaluate, simultaneously, the volume ratio at zero pressure, N.

The general expression for the Burnett experiment is of the form

$$Z_r = (Z_o/P_o)\, f_r\, N^r\, P_r \tag{1}$$

where Z_r is the compressibility factor of the gas at pressure P_r and Z_o is the corresponding value at pressure P_o; N is the ratio of the volumes of both containers at zero pressure to that of the first container at zero pressure; r is the expansion number; P_r is the equilibrium pressure after the r^{th} expansion; P_o is the initial pressure;

$$f_r = \frac{(1+\alpha P_1)\,(1+\alpha P_2)\,\ldots\,(1+\alpha P_r)}{(1+\beta P_o)\,(1+\beta P_1)\,\ldots\,(1+\beta P_{r-1})};$$

α is the pressure coefficient of the volume of both containers; and β is the pressure coefficient of the volume of the first container. The pressures are expressed in either psia or standard atmosphere units and are calculated by the method previously outlined (_7_),[2/]

_2_/ Underlined numbers in parentheses refer to items in the list of references at the end of this report.

which is based on a general program developed for this particular purpose (5).

In this report, we assume Z_r is a function of the second and third virial coefficients and is expressible in terms of a Berlin expansion in powers of P_r,

$$Z_r = 1 + BP_r + CP_r^2 . \quad (2)$$

For the interested reader, a more detailed discussion of the case where Z_r is of some other functional form than that given by equation (2) or where Z_r is an explicit function of the molal density, ρ_r, in which case Z_r is to be considered an implicit function of P_r, is given in (2).

f_r of equation (1) is a function of all of the observed pressures but is completely independent of the pressure distortion coefficients of the bombs which have been previously determined. The principles connected with the evaluation of α and β have been given by Briggs (5, 6) and, therefore, will not be repeated in this report.

Statistical tests were carried out on the experimental compressibility data on helium at 0° C for run number 3 obtained by Briggs (5) in order to illustrate: 1. the effect an error in the determination of the distortion coefficients of the high-pressure containers with pressure produces in the compressibility factor, Z, which is a function of B and C, and in the volume ratio at zero pressure, N; 2. the effect an error in the fractional change in the effective area of the piston (at 25° C, P=0) with pressure introduces in Z and N; and 3. the effect an error of ignoring the pressure distortion of the bombs induces in Z and N.

The parameters of equation (1), assuming Z_r to be expressible by equation (2), were evaluated by the method outlined in (2), which is based on the general non-linear least squares problem developed for this particular problem (1, 3, 4, 8). The calculations and results of the statistical tests on the experimental PVT data for helium at 0° C for run number 3 reported in (5) are given in the following sections.

THE EFFECT AN ERROR IN THE DETERMINATION OF α AND β PRODUCES IN Z, B, C, AND N

The experimental results of Briggs' (5) compressibility measurements on helium at 0° C for run number 3 are given in table 1 of this report. The values of column 1 are expansion numbers corresponding to the observed pressures of column 2. The pressures are in standard atmosphere units and the number after the letter E merely indicates the power of 10 by which each pressure is multiplied.

Equation (1),

$$Z_r = (Z_o/P_o)\, f_r\, N^r\, P_r\ , \tag{1}$$

was applied to the data of table 1 assuming Z_r to be of the form as given by equation (2),

$$Z_r = 1 + BP_r + CP_r^2\ . \tag{2}$$

The values of the pressure distortion coefficients of the high-pressure bombs were taken to be (5, 6):

$$\alpha\ (0°\ C) = 1.6678 \times 10^{-6}\ atm^{-1}\ , \tag{3}$$

$$\beta\ (0°\ C) = 1.6671 \times 10^{-6}\ atm^{-1}\ . \tag{4}$$

TABLE 1.-Original experimental observations on helium at 0° C for run number 3 as reported by Briggs (5)

$$Z_r = (Z_o/P_o) f_r N^r P_r, \; P_r \text{ in atm}$$

$$Z_r = 1 + BP_r + CP_r^2$$

$$\alpha = 1.6678 \times 10^{-6} \text{ atm}^{-1}$$

$$\beta = 1.6671 \times 10^{-6} \text{ atm}^{-1}$$

$$b^{1/} = -3.50 \times 10^{-8} \text{ in}^2/\text{in}^2 \text{ psi}$$

r	$P_{r(obs)}$
0	7.0128236E02
1	3.0170799E02
2	1.4061376E02
3	6.8033559E01
4	3.3517320E01
5	1.6660572E01
6	8.3186011E00
7	4.1639855E00

1/ b is the fractional change in the effective area of the piston (at 25° C, P=0) with pressure. This value was supplied by the Ruska Instrument Corporation; see (5) and (7) for a more detailed discussion of this constant.

The three parameters of equation (1), B, C, and N, were evaluated by an iteration technique (2) to give the results reported in table 2 of this report, assuming α and β to be defined by equations (3) and (4), respectively. The values of column 1 of this table are expansion numbers corresponding to the observed pressures of column 2. The pressures of column 3 are those pressures which exactly satisfy equation (1). Column 4 is the residual of $P_{r(obs)}$ and is just the difference of columns 2 and 3. The relative error of the observed pressure, column 5, is just column 4 divided by column 2.

The best estimates of the unknown parameters of equation (1) are also included in table 2 along with the best estimate of the uncertainty of each of these quantities. The best values for B, C, and N were taken to be the least squares values, where the observed pressures were taken to be of equal reliability. The quantities S_N, S_B, and S_C are the calculated standard errors of N, B, and C evaluated by the method outlined in (8). The quantities given under the heading VARIANCES AND COVARIANCES are just variances and covariances of the parameters calculated by the method outlined in (8) (i.e., S2N is the variance of N; S2BC is the covariance of BC; etc.).

From the data of table 2 and equation (2), the compressibility factors of table 3 were calculated, together with the standard deviation of each Z. The values of column 1 of this table are nominal pressures in standard atmosphere units. Column 2 gives values of Z corresponding to the pressures of column 1, while the standard deviations of these compressibility factors, SZ, are given in column 3.

TABLE 2.-Results of the analysis of the data of table 1 for α and β defined by equations (3) and (4)

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	(P,OBS.-P,CAL.)/P,OBS.
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-4.99133E-04	-1.65435E-06
2	1.4061376E&02	1.4061112E&02	2.64039E-03	1.87776E-05
3	6.8033559E&01	6.8037124E&01	-3.56490E-03	-5.23991E-05
4	3.3517320E&01	3.3518813E&01	-1.49289E-03	-4.45411E-05
5	1.6660572E&01	1.6659332E&01	1.23916E-03	7.43771E-05
6	8.3186011E-00	8.3161327E-00	2.46844E-03	2.96737E-04
7	4.1639855E-00	4.1603444E-00	3.64111E-03	8.74430E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30445E-05

CONSTANTS AND STANDARD ERRORS

N	1.994559047E-00	SN	1.29990E-04
B	5.277062588E-04	SB	8.84365E-07
C	-4.739061450E-08	SC	5.96411E-10

VARIANCES AND COVARIANCES

S2N	1.68975E-08
S2B	7.82102E-13
S2C	3.55707E-19
S2BC	-5.22569E-16
S2BN	-1.10699E-10
S2CN	7.13077E-14

TABLE 3.-Compressibility factors for helium at 0° C as a function of pressure, evaluated from equation (2) and the B and C values of table 2

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005276588E-00	1.05758E-06
2.000E-00	1.0010552229E-00	2.04752E-06
5.000E-00	1.0026373465E-00	4.89493E-06
1.000E&01	1.0052723235E-00	9.44892E-06
2.500E&01	1.0131630373E-00	2.24701E-05
5.000E&01	1.0262668364E-00	4.30866E-05
7.500E&01	1.0393113972E-00	6.28415E-05
1.000E&02	1.0522967197E-00	8.19129E-05
1.250E&02	1.0652228039E-00	1.00365E-04
1.500E&02	1.0780896499E-00	1.18224E-04
2.000E&02	1.1036456271E-00	1.52167E-04
2.500E&02	1.1289646512E-00	1.83675E-04
3.000E&02	1.1540467223E-00	2.12614E-04
3.500E&02	1.1788918403E-00	2.38822E-04
4.000E&02	1.2035000052E-00	2.62127E-04
4.500E&02	1.2278712170E-00	2.82357E-04
5.000E&02	1.2520054757E-00	2.99346E-04
6.000E&02	1.2995631340E-00	3.22985E-04
7.000E&02	1.3461729800E-00	3.31965E-04
8.000E&02	1.3918350137E-00	3.25547E-04
9.000E&02	1.4365492351E-00	3.03584E-04
1.000E&03	1.4803156442E-00	2.67134E-04

Now suppose the determinations of the pressure distortion coefficients of the high-pressure containers are in error - this is not to imply or be construed to mean that α and β are incorrect! However, to illustrate the first statistical test carried out on the 0° C helium data for run number 3, we assume these quantities to be in error by some amount. Then on solving equation (1), we would get new values for B, C, and N as well as new values of Z. The problem, therefore, is to reevaluate these parameters and compressibility factors and to decide whether the effect an error in α and β produces a statistically significant difference in the values of B, C, N, and Z.

Let us assume errors in α and β of ±10% and ±20%:

$$0.8\,\alpha = 1.33424 \times 10^{-6}\ \text{atm}^{-1}, \quad 0.8\,\beta = 1.33368 \times 10^{-6}\ \text{atm}^{-1};$$

$$0.9\,\alpha = 1.50102 \times 10^{-6}\ \text{atm}^{-1}, \quad 0.9\,\beta = 1.50039 \times 10^{-6}\ \text{atm}^{-1};$$

$$1.1\,\alpha = 1.83458 \times 10^{-6}\ \text{atm}^{-1}, \quad 1.1\,\beta = 1.83381 \times 10^{-6}\ \text{atm}^{-1};$$

$$1.2\,\alpha = 2.00136 \times 10^{-6}\ \text{atm}^{-1}, \quad 1.2\,\beta = 2.00052 \times 10^{-6}\ \text{atm}^{-1}.$$

Table 4 of this report gives the results of the new values of the parameters assuming errors in α and in β of ±10% and ±20%. The values given in table 4 have the same meaning as those of table 2. From the results given in table 4, the compressibility factors of table 5 were calculated, together with the uncertainty of each Z factor.

From the data given in tables 1, 2, 3, 4, and 5 of this report, the following significant results indicate that:

1. Even if the determination of the pressure distortion coefficients of the bombs is in error by as much as ±20%, the least squares

Now suppose the determinations of the pressure distortion coefficients of the high-pressure containers are in error - this is not to imply or be construed to mean that α and β are incorrect! However, to illustrate the first statistical test carried out on the 0° C helium data for run number 3, we assume these quantities to be in error by some amount. Then on solving equation (4), we would get new values for B, C, and N as well as new values of Z. The problem, therefore, is to reevaluate these parameters and compressibility factors and to decide whether the effect an error in α and β produces a statistically significant difference in the values of B, C, N, and Z.

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$$1.1\,\alpha = 1.83458 \times 10^{-6}\ \text{atm}^{-1},\quad 1.1\,\beta = 1.83381 \times 10^{-6}\ \text{atm}^{-1};$$

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1. Even if the determination of the pressure distortion coefficients of the bombs is in error by as much as ±20%, the least squares

TABLE 4.-Results of the analysis of the data of table 1 assuming errors in α and β of ±10% and ±20%

$0.8\alpha = 1.33424 \times 10^{-6}$ atm^{-1} $0.8\beta = 1.33368 \times 10^{-6}$ atm^{-1}

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	(P,OBS.-P,CAL.)/P,OBS.
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-4.99511E-04	-1.65561E-06
2	1.4061376E&02	1.4061112E&02	2.64261E-03	1.87934E-05
3	6.8033559E&01	6.8037128E&01	-3.56832E-03	-5.24494E-05
4	3.3517320E&01	3.3518814E&01	-1.49367E-03	-4.45641E-05
5	1.6660572E&01	1.6659331E&01	1.24067E-03	7.44677E-05
6	8.3186011E-00	8.3161305E-00	2.47058E-03	2.96995E-04
7	4.1639855E-00	4.1603425E-00	3.64300E-03	8.74884E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.31114E-05

CONSTANTS AND STANDARD ERRORS

N	1.994559505E-00	SN	1.30086E-04
B	5.273648758E-04	SB	8.84952E-07
C	-4.754640934E-08	SC	5.96924E-10

VARIANCES AND COVARIANCES

S2N	1.69224E-08
S2B	7.83141E-13
S2C	3.56319E-19
S2BC	-5.23370E-16
S2BN	-1.10854E-10
S2CN	7.14232E-14

TABLE 4.-Results of the analysis of the data of table 1 assuming errors in α and β of ±10% and ±20% (Con.)

$0.9\alpha = 1.50102 \times 10^{-6}\ atm^{-1}$ $0.9\beta = 1.50039 \times 10^{-6}\ atm^{-1}$

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	P,OBS.-P,CAL. / P,OBS.
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-4.99322E-04	-1.65498E-06
2	1.4061376E&02	1.4061112E&02	2.64150E-03	1.87855E-05
3	6.8033559E&01	6.8037126E&01	-3.56661E-03	-5.24243E-05
4	3.3517320E&01	3.3518813E&01	-1.49328E-03	-4.45526E-05
5	1.6660572E&01	1.6659332E&01	1.23992E-03	7.44224E-05
6	8.3186011E-00	8.3161316E-00	2.46951E-03	2.96866E-04
7	4.1639855E-00	4.1603434E-00	3.64206E-03	8.74657E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30780E-05

CONSTANTS AND STANDARD ERRORS

N	1.994559276E-00	SN	1.30038E-04
B	5.275355672E-04	SB	8.84659E-07
C	-4.746851200E-08	SC	5.96668E-10

VARIANCES AND COVARIANCES

S2N	1.69100E-08
S2B	7.82621E-13
S2C	3.56013E-19
S2BC	-5.22969E-16
S2BN	-1.10777E-10
S2CN	7.13654E-14

TABLE 4.-Results of the analysis of the data of table 1 assuming errors in α and β of ±10% and ±20% (Con.)

$1.1\alpha = 1.83458 \times 10^{-6}\ \mathrm{atm}^{-1}$ $1.1\beta = 1.83381 \times 10^{-6}\ \mathrm{atm}^{-1}$

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	(P,OBS.-P,CAL.)/P,OBS.
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-4.98944E-04	-1.65373E-06
2	1.4061376E&02	1.4061112E&02	2.63928E-03	1.87697E-05
3	6.8033559E&01	6.8037123E&01	-3.56319E-03	-5.23740E-05
4	3.3517320E&01	3.3518812E&01	-1.49251E-03	-4.45296E-05
5	1.6660572E&01	1.6659333E&01	1.23841E-03	7.43318E-05
6	8.3186011E-00	8.3161337E-00	2.46737E-03	2.96608E-04
7	4.1639855E-00	4.1603453E-00	3.64016E-03	8.74202E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30111E-05

CONSTANTS AND STANDARD ERRORS

N	1.994558817E-00	SN	1.29942E-04
B	5.278769505E-04	SB	8.84071E-07
C	-4.731271686E-08	SC	5.96155E-10

VARIANCES AND COVARIANCES

S2N	1.68850E-08
S2B	7.81583E-13
S2C	3.55401E-19
S2BC	-5.22169E-16
S2BN	-1.10622E-10
S2CN	7.12500E-14

TABLE 4.-Results of the analysis of the data of table 1 assuming errors in α and β of ±10% and ±20% (Con.)

$1.2\alpha = 2.00136 \times 10^{-6}$ atm^{-1} $\quad$ $1.2\beta = 2.00052 \times 10^{-6}$ atm^{-1}

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	(P,OBS.-P,CAL.)/P,OBS.
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-4.98754E-04	-1.65310E-06
2	1.4061376E&02	1.4061112E&02	2.63817E-03	1.87618E-05
3	6.8033559E&01	6.8037121E&01	-3.56148E-03	-5.23489E-05
4	3.3517320E&01	3.3518812E&01	-1.49212E-03	-4.45181E-05
5	1.6660572E&01	1.6659334E&01	1.23765E-03	7.42865E-05
6	8.3186011E-00	8.3161348E-00	2.46629E-03	2.96479E-04
7	4.1639855E-00	4.1603463E-00	3.63922E-03	8.73975E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.29777E-05

CONSTANTS AND STANDARD ERRORS

N	1.994558588E-00	SN	1.29894E-04
B	5.280476424E-04	SB	8.83778E-07
C	-4.723481905E-08	SC	5.95898E-10

VARIANCES AND COVARIANCES

S2N	1.68726E-08
S2B	7.81063E-13
S2C	3.55095E-19
S2BC	-5.21769E-16
S2BN	-1.10544E-10
S2CN	7.11924E-14

TABLE 5.-Compressibility factors for helium at 0° C evaluated from the B and C values of table 4 and equation (2)

$0.8\alpha = 1.33424 \times 10^{-6}\ \mathrm{atm}^{-1}$ $\qquad$ $0.8\beta = 1.33368 \times 10^{-6}\ \mathrm{atm}^{-1}$

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005273173E-00	1.05818E-06
2.000E-00	1.0010545395E-00	2.04872E-06
5.000E-00	1.0026356357E-00	4.89791E-06
1.000E&01	1.0052688941E-00	9.45481E-06
2.500E&01	1.0131544053E-00	2.24846E-05
5.000E&01	1.0262493777E-00	4.31147E-05
7.500E&01	1.0392849171E-00	6.28827E-05
1.000E&02	1.0522610234E-00	8.19665E-05
1.250E&02	1.0651776968E-00	1.00431E-04
1.500E&02	1.0780349371E-00	1.18301E-04
2.000E&02	1.1035711187E-00	1.52264E-04
2.500E&02	1.1288695683E-00	1.83790E-04
3.000E&02	1.1539302859E-00	2.12744E-04
3.500E&02	1.1787532713E-00	2.38965E-04
4.000E&02	1.2033385248E-00	2.62280E-04
4.500E&02	1.2276860462E-00	2.82518E-04
5.000E&02	1.2517958355E-00	2.99512E-04
6.000E&02	1.2993022181E-00	3.23153E-04
7.000E&02	1.3458576724E-00	3.32126E-04
8.000E&02	1.3914621986E-00	3.25693E-04
9.000E&02	1.4361157966E-00	3.03709E-04
1.000E&03	1.4798184664E-00	2.67233E-04

TABLE 5.-Compressibility factors for helium at 0° C evaluated from the B and C values of table 4 and equation (2) (Con.)

$0.9\alpha = 1.50102 \times 10^{-6}$ atm^{-1} $\quad 0.9\beta = 1.50039 \times 10^{-6}$ atm^{-1}

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005274880E-00	1.05788E-06
2.000E-00	1.0010548812E-00	2.04812E-06
5.000E-00	1.0026364911E-00	4.89642E-06
1.000E&01	1.0052706088E-00	9.45187E-06
2.500E&01	1.0131587213E-00	2.24774E-05
5.000E&01	1.0262581070E-00	4.31006E-05
7.500E&01	1.0392981571E-00	6.28621E-05
1.000E&02	1.0522788716E-00	8.19397E-05
1.250E&02	1.0652002504E-00	1.00398E-04
1.500E&02	1.0780622935E-00	1.18262E-04
2.000E&02	1.1036083729E-00	1.52215E-04
2.500E&02	1.1289171098E-00	1.83732E-04
3.000E&02	1.1539885040E-00	2.12679E-04
3.500E&02	1.1788225558E-00	2.38894E-04
4.000E&02	1.2034192649E-00	2.62204E-04
4.500E&02	1.2277786315E-00	2.82437E-04
5.000E&02	1.2519006556E-00	2.99429E-04
6.000E&02	1.2994326760E-00	3.23069E-04
7.000E&02	1.3460153261E-00	3.32045E-04
8.000E&02	1.3916486060E-00	3.25620E-04
9.000E&02	1.4363325157E-00	3.03647E-04
1.000E&03	1.4800670552E-00	2.67183E-04

TABLE 5.-Compressibility factors for helium at 0° C evaluated from the B and C values of table 4 and equation (2) (Con.)

$1.1\alpha = 1.83458 \times 10^{-6}\ \mathrm{atm}^{-1}$ $1.1\beta = 1.83381 \times 10^{-6}\ \mathrm{atm}^{-1}$

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005278296E-00	1.05728E-06
2.000E-00	1.0010555646E-00	2.04692E-06
5.000E-00	1.0026382019E-00	4.89345E-06
1.000E&01	1.0052740382E-00	9.44598E-06
2.500E&01	1.0131673533E-00	2.24629E-05
5.000E&01	1.0262755657E-00	4.30725E-05
7.500E&01	1.0393246372E-00	6.28209E-05
1.000E&02	1.0523145678E-00	8.18861E-05
1.250E&02	1.0652453576E-00	1.00333E-04
1.500E&02	1.0781170064E-00	1.18186E-04
2.000E&02	1.1036828814E-00	1.52118E-04
2.500E&02	1.1290121928E-00	1.83618E-04
3.000E&02	1.1541049406E-00	2.12549E-04
3.500E&02	1.1789611248E-00	2.38751E-04
4.000E&02	1.2035807455E-00	2.62051E-04
4.500E&02	1.2279638025E-00	2.82277E-04
5.000E&02	1.2521102960E-00	2.99264E-04
6.000E&02	1.2996935922E-00	3.22901E-04
7.000E&02	1.3463306341E-00	3.31884E-04
8.000E&02	1.3920214216E-00	3.25474E-04
9.000E&02	1.4367659548E-00	3.03522E-04
1.000E&03	1.4805642336E-00	2.67084E-04

TABLE 5.-Compressibility factors for helium at 0° C evaluated from the B and C values of table 4 and equation (2) (Con.)

$1.2\alpha = 2.00136 \times 10^{-6}$ atm^{-1} $\quad$ $1.2\beta = 2.00052 \times 10^{-6}$ atm^{-1}

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005280004E-00	1.05698E-06
2.000E-00	1.0010559063E-00	2.04632E-06
5.000E-00	1.0026390573E-00	4.89196E-06
1.000E&01	1.0052757529E-00	9.44303E-06
2.500E&01	1.0131716692E-00	2.24557E-05
5.000E&01	1.0262842950E-00	4.30584E-05
7.500E&01	1.0393378773E-00	6.28003E-05
1.000E&02	1.0523324160E-00	8.18593E-05
1.250E&02	1.0652679112E-00	1.00300E-04
1.500E&02	1.0781443629E-00	1.18148E-04
2.000E&02	1.1037201357E-00	1.52070E-04
2.500E&02	1.1290597344E-00	1.83560E-04
3.000E&02	1.1541631590E-00	2.12484E-04
3.500E&02	1.1790304095E-00	2.38679E-04
4.000E&02	1.2036614859E-00	2.61974E-04
4.500E&02	1.2280563882E-00	2.82197E-04
5.000E&02	1.2522151164E-00	2.99181E-04
6.000E&02	1.2998240506E-00	3.22817E-04
7.000E&02	1.3464882883E-00	3.31804E-04
8.000E&02	1.3922078297E-00	3.25401E-04
9.000E&02	1.4369826747E-00	3.03459E-04
1.000E&03	1.4808128234E-00	2.67034E-04

solution for the volume ratio at zero pressure, N, is not significantly affected. We conclude, therefore, that errors of as much as ±20% in the determination of α and β produce insignificant differences in the least squares solution of N.

2. The least squares solutions for the second and third virial coefficients, B and C, assuming errors of as much as ±20% in the pressure distortion coefficients, differ from those evaluated for $1.0\ \alpha = 1.6678 \times 10^{-6}\ \text{atm}^{-1}$ and $1.0\ \beta = 1.6671 \times 10^{-6}\ \text{atm}^{-1}$ by less than the uncertainty with which we know these quantities. This is interpreted to mean that a ±20% error in the determination of the pressure distortion coefficients of the bombs produces differences in the least squares solutions of B and of C which are statistically insignificant.

3. The values of the compressibility factor differ by no more than the stated deviations of these Z's for the five solutions: $0.8\ \alpha$; $0.9\ \alpha$; $1.0\ \alpha$; $1.1\ \alpha$; $1.2\ \alpha$. We conclude, therefore, that errors of this magnitude in α and β produce differences in Z which are no greater than the calculated uncertainties with which we know these quantities.

One of the important points to come out of this analysis, which I had not appreciated before, is that the independently determined values of the pressure distortion coefficients of the bombs apparently have little influence on the precision of the PVT data obtained from a Burnett compressibility apparatus. This means, therefore, that <u>any</u> error in the determination of α and β should not significantly influence the <u>internal</u> precision of compressibility measurements on

the gas. This has been found to be true in the analysis of the 0° C helium isotherm data of Briggs (5) for run number 3.

THE EFFECT AN ERROR IN THE FRACTIONAL CHANGE IN THE EFFECTIVE AREA OF THE PISTON (AT 25° C, P=0) WITH PRESSURE PRODUCES IN Z, B, C, AND N

To illustrate better the second statistical test applied to the experimental results reported in (5), the expression from which pressures are calculated (7) is introduced:

$$P_g = \frac{M_a (1 - \rho_a/\rho_b)\, g_L/g_S}{A_o (1 + bP_g)[1 + c(t-25)]}, \tag{5}$$

where

P_g = calculated gage pressure (5, 7), psig,

M_a = apparent mass, as determined by comparison with brass standards, in air, lb,

ρ_a = density of air, g/cc,

ρ_b = density of brass, g/cc,

g_L = local acceleration due to gravity, gal,

g_S = standard acceleration due to gravity, gal,

A_o = effective area of piston (at 25° C, P=0), in^2,

b = fractional change in A_o with pressure, in^2/in^2 psi,

c = temperature coefficient of linear expansion of the piston-cylinder combination, in/in °C, and

t = temperature of the piston-cylinder, °C.

Suppose the value of b is in error by some amount. Then the pressures as calculated from equation (5) would be different and, hence, we would get new values for B, C, and N as well as new values for the compressibility factor. The problem is to determine the effect an error in b produces in the volume ratio at zero pressure, the virial coefficients, and the compressibility factor and to decide whether this error is statisticallly significant.

Let us assume the fractional change in the effective area of the piston (at 25° C, P=0) with pressure to be in error ±10% and ±20%:

$$0.8\ b = -2.80 \times 10^{-8}\ psi^{-1};$$

$$0.9\ b = -3.15 \times 10^{-8}\ psi^{-1};$$

$$1.1\ b = -3.85 \times 10^{-8}\ psi^{-1};$$

$$1.2\ b = -4.20 \times 10^{-8}\ psi^{-1}.$$

Table 6 of this report gives the new values for the pressures as determined from the solution of equation (5) using the method outlined in (5) and (7). All pressures are expressed in standard atmosphere units. The values of column 1 of this table are expansion numbers corresponding to the observed pressures of columns 2, 3, 4, and 5.

Equation (1) was applied to the data of table 6, assuming Z_r to be expressible by equation (2). Table 7 of this report gives the results of the analysis of the data of table 6 for α and β defined by equations (3) and (4), where the quantities given in this table have the same meaning as those of table 2. From the values of B and C of table 7, the compressibility factors of table 8 were calculated.

TABLE 6.-Experimental pressures, in standard atmosphere units, as evaluated from equation (5), assuming the fractional change in the effective area of the piston (at 25° C, P=0) to be in error ±10% and ±20%

r	$P_{r(obs)}$ 1/	$P_{r(obs)}$ 2/	$P_{r(obs)}$ 3/	$P_{r(obs)}$ 4/
0	7.0123187E02	7.0125711E02	7.0130761E02	7.0133287E02
1	3.0169868E02	3.0170334E02	3.0171265E02	3.0171731E02
2	1.4061175E02	1.4061276E02	1.4061477E02	1.4061577E02
3	6.8033095E01	6.8033327E01	6.8033791E01	6.8034023E01
4	3.3517210E01	3.3517265E01	3.3517375E01	3.3517429E01
5	1.6660546E01	1.6660559E01	1.6660584E01	1.6660597E01
6	8.3185954E00	8.3185983E00	8.3186040E00	8.3186068E00
7	4.1639844E00	4.1639849E00	4.1639860E00	4.1639866E00

1/ Pressures as calculated by the method outlined in (5) and (7), assuming b to be in error by -20%.
2/ Pressures as calculated by the method outlined in (5) and (7), assuming b to be in error by -10%.
3/ Pressures as calculated by the method outlined in (5) and (7), assuming b to be in error by +10%.
4/ Pressures as calculated by the method outlined in (5) and (7), assuming b to be in error by +20%.

TABLE 7.-Results of the analysis of the data of table 6 for α and β defined by equations (3) and (4)

$$0.8b = -2.80 \times 10^{-8} \text{ psi}^{-1}$$

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	P,OBS.-P,CAL. / P,OBS.
0	7.0123187E&02	7.0123187E&02	0.00000E-99	0.00000E-99
1	3.0169868E&02	3.0169918E&02	-4.99031E-04	-1.65407E-06
2	1.4061175E&02	1.4060911E&02	2.63970E-03	1.87729E-05
3	6.8033095E&01	6.8036659E&01	-3.56376E-03	-5.23828E-05
4	3.3517210E&01	3.3518703E&01	-1.49266E-03	-4.45341E-05
5	1.6660546E&01	1.6659307E&01	1.23865E-03	7.43466E-05
6	8.3185954E-00	8.3161277E-00	2.46771E-03	2.96651E-04
7	4.1639844E-00	4.1603439E-00	3.64045E-03	8.74273E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30223E-05

CONSTANTS AND STANDARD ERRORS

N	1.994558905E-00	SN	1.29960E-04
B	5.276058057E-04	SB	8.84184E-07
C	-4.739691916E-08	SC	5.96346E-10

VARIANCES AND COVARIANCES

S2N	1.68896E-08
S2B	7.81781E-13
S2C	3.55628E-19
S2BC	-5.22405E-16
S2BN	-1.10651E-10
S2CN	7.12832E-14

TABLE 7.-Results of the analysis of the data of table 6 for α and β defined by equations (3) and (4) (Con.)

$$0.9b = -3.15 \times 10^{-8} \text{ psi}^{-1}$$

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	(P,OBS.-P,CAL.)/P,OBS.
0	7.0125711E&02	7.0125711E&02	0.00000E-99	0.00000E-99
1	3.0170334E&02	3.0170383E&02	-4.99082E-04	-1.65421E-06
2	1.4061276E&02	1.4061012E&02	2.64005E-03	1.87753E-05
3	6.8033327E&01	6.8036892E&01	-3.56433E-03	-5.23910E-05
4	3.3517265E&01	3.3518758E&01	-1.49277E-03	-4.45376E-05
5	1.6660559E&01	1.6659320E&01	1.23891E-03	7.43619E-05
6	8.3185983E-00	8.3161302E-00	2.46808E-03	2.96694E-04
7	4.1639849E-00	4.1603441E-00	3.64078E-03	8.74351E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30334E-05

CONSTANTS AND STANDARD ERRORS

N	1.994558976E-00	SN	1.29975E-04
B	5.276560323E-04	SB	8.84274E-07
C	-4.739376953E-08	SC	5.96378E-10

VARIANCES AND COVARIANCES

S2N	1.68936E-08
S2B	7.81942E-13
S2C	3.55667E-19
S2BC	-5.22487E-16
S2BN	-1.10675E-10
S2CN	7.12955E-14

TABLE 7.-Results of the analysis of the data of table 6 for α and β defined by equations (3) and (4) (Con.)

$$1.1b = -3.85 \times 10^{-8} \text{ psi}^{-1}$$

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	(P,OBS.-P,CAL.)/P,OBS.
0	7.0130761E&02	7.0130761E&02	0.00000E-99	0.00000E-99
1	3.0171265E&02	3.0171315E&02	-4.99183E-04	-1.65450E-06
2	1.4061477E&02	1.4061213E&02	2.64074E-03	1.87799E-05
3	6.8033791E&01	6.8037357E&01	-3.56547E-03	-5.24073E-05
4	3.3517375E&01	3.3518868E&01	-1.49301E-03	-4.45446E-05
5	1.6660584E&01	1.6659345E&01	1.23942E-03	7.43923E-05
6	8.3186040E-00	8.3161352E-00	2.46880E-03	2.96781E-04
7	4.1639860E-00	4.1603446E-00	3.64144E-03	8.74508E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30556E-05

CONSTANTS AND STANDARD ERRORS

N	1.994559117E-00	SN	1.30005E-04
B	5.277564850E-04	SB	8.84456E-07
C	-4.738745396E-08	SC	5.96444E-10

VARIANCES AND COVARIANCES

S2N	1.69015E-08
S2B	7.82262E-13
S2C	3.55746E-19
S2BC	-5.22652E-16
S2BN	-1.10724E-10
S2CN	7.13200E-14

TABLE 7.-Results of the analysis of the data of table 6 for α and β defined by equations (3) and (4) (Con.)

$$1.2b = -4.20 \times 10^{-8} \text{ psi}^{-1}$$

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	(P,OBS.-P,CAL.)/P,OBS.
0	7.0133287E&02	7.0133287E&02	0.00000E-99	0.00000E-99
1	3.0171731E&02	3.0171780E&02	-4.99234E-04	-1.65464E-06
2	1.4061577E&02	1.4061313E&02	2.64109E-03	1.87823E-05
3	6.8034023E&01	6.8037589E&01	-3.56604E-03	-5.24155E-05
4	3.3517429E&01	3.3518923E&01	-1.49313E-03	-4.45481E-05
5	1.6660597E&01	1.6659357E&01	1.23967E-03	7.44075E-05
6	8.3186068E-00	8.3161377E-00	2.46916E-03	2.96824E-04
7	4.1639866E-00	4.1603448E-00	3.64176E-03	8.74586E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.30667E-05

CONSTANTS AND STANDARD ERRORS

N	1.994559188E-00	SN	1.30021E-04
B	5.278067112E-04	SB	8.84546E-07
C	-4.738428794E-08	SC	5.96477E-10

VARIANCES AND COVARIANCES

S2N	1.69054E-08
S2B	7.82423E-13
S2C	3.55785E-19
S2BC	-5.22734E-16
S2BN	-1.10748E-10
S2CN	7.13323E-14

TABLE 8.-Compressibility factors for helium at 0° C evaluated from the data of table 7 and equation (2)

$$0.8b = -2.80 \times 10^{-8}\ psi^{-1}$$

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005275584E-00	1.05732E-06
2.000E-00	1.0010550220E-00	2.04704E-06
5.000E-00	1.0026368441E-00	4.89381E-06
1.000E&01	1.0052713183E-00	9.44682E-06
2.500E&01	1.0131605220E-00	2.24653E-05
5.000E&01	1.0262617979E-00	4.30775E-05
7.500E&01	1.0393038277E-00	6.28283E-05
1.000E&02	1.0522866113E-00	8.18957E-05
1.250E&02	1.0652101488E-00	1.00344E-04
1.500E&02	1.0780744401E-00	1.18199E-04
2.000E&02	1.1036252843E-00	1.52134E-04
2.500E&02	1.1289391439E-00	1.83634E-04
3.000E&02	1.1540160190E-00	2.12566E-04
3.500E&02	1.1788559094E-00	2.38766E-04
4.000E&02	1.2034588152E-00	2.62064E-04
4.500E&02	1.2278247364E-00	2.82287E-04
5.000E&02	1.2519536730E-00	2.99270E-04
6.000E&02	1.2995005925E-00	3.22897E-04
7.000E&02	1.3460995736E-00	3.31867E-04
8.000E&02	1.3917506163E-00	3.25443E-04
9.000E&02	1.4364537206E-00	3.03477E-04
1.000E&03	1.4802088865E-00	2.67028E-04

TABLE 8.-Compressibility factors for helium at 0° C evaluated from the data of table 7 and equation (2) (Con.)

$$0.9b = -3.15 \times 10^{-8} \text{ psi}^{-1}$$

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005276086E-00	1.05745E-06
2.000E-00	1.0010551224E-00	2.04728E-06
5.000E-00	1.0026370953E-00	4.89437E-06
1.000E&01	1.0052718209E-00	9.44787E-06
2.500E&01	1.0131617797E-00	2.24677E-05
5.000E&01	1.0262643171E-00	4.30820E-05
7.500E&01	1.0393076124E-00	6.28349E-05
1.000E&02	1.0522916655E-00	8.19043E-05
1.250E&02	1.0652164763E-00	1.00355E-04
1.500E&02	1.0780820450E-00	1.18211E-04
2.000E&02	1.1036354556E-00	1.52150E-04
2.500E&02	1.1289518974E-00	1.83655E-04
3.000E&02	1.1540313704E-00	2.12590E-04
3.500E&02	1.1788738745E-00	2.38794E-04
4.000E&02	1.2034794098E-00	2.62096E-04
4.500E&02	1.2278479762E-00	2.82322E-04
5.000E&02	1.2519795737E-00	2.99308E-04
6.000E&02	1.2995318623E-00	3.22941E-04
7.000E&02	1.3461362755E-00	3.31916E-04
8.000E&02	1.3917928133E-00	3.25495E-04
9.000E&02	1.4365014757E-00	3.03530E-04
1.000E&03	1.4802622627E-00	2.67081E-04

TABLE 8.-Compressibility factors for helium at 0° C evaluated from the data of table 7 and equation (2) (Con.)

$$1.1b = -3.85 \times 10^{-8} \text{ psi}^{-1}$$

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005277090E-00	1.05771E-06
2.000E-00	1.0010553234E-00	2.04777E-06
5.000E-00	1.0026375977E-00	4.89549E-06
1.000E&01	1.0052728261E-00	9.44997E-06
2.500E&01	1.0131642949E-00	2.24726E-05
5.000E&01	1.0262693556E-00	4.30911E-05
7.500E&01	1.0393151819E-00	6.28481E-05
1.000E&02	1.0523017739E-00	8.19215E-05
1.250E&02	1.0652291316E-00	1.00376E-04
1.500E&02	1.0780972550E-00	1.18237E-04
2.000E&02	1.1036557988E-00	1.52183E-04
2.500E&02	1.1289774054E-00	1.83695E-04
3.000E&02	1.1540620746E-00	2.12639E-04
3.500E&02	1.1789098066E-00	2.38850E-04
4.000E&02	1.2035206014E-00	2.62159E-04
4.500E&02	1.2278944588E-00	2.82392E-04
5.000E&02	1.2520313790E-00	2.99385E-04
6.000E&02	1.2995944076E-00	3.23030E-04
7.000E&02	1.3462096871E-00	3.32014E-04
8.000E&02	1.3918772175E-00	3.25599E-04
9.000E&02	1.4365969988E-00	3.03638E-04
1.000E&03	1.4803690311E-00	2.67187E-04

TABLE 8.-Compressibility factors for helium at 0° C evaluated from the data of table 7 and equation (2) (Con.)

$$1.2b = -4.20 \times 10^{-8} \text{ psi}^{-1}$$

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005277593E-00	1.05784E-06
2.000E-00	1.0010554238E-00	2.04801E-06
5.000E-00	1.0026378489E-00	4.89605E-06
1.000E&01	1.0052733286E-00	9.45102E-06
2.500E&01	1.0131655526E-00	2.24750E-05
5.000E&01	1.0262718748E-00	4.30957E-05
7.500E&01	1.0393189667E-00	6.28547E-05
1.000E&02	1.0523068282E-00	8.19301E-05
1.250E&02	1.0652354594E-00	1.00387E-04
1.500E&02	1.0781048602E-00	1.18249E-04
2.000E&02	1.1036659707E-00	1.52200E-04
2.500E&02	1.1289901598E-00	1.83716E-04
3.000E&02	1.1540774274E-00	2.12663E-04
3.500E&02	1.1789277736E-00	2.38878E-04
4.000E&02	1.2035411984E-00	2.62190E-04
4.500E&02	1.2279177017E-00	2.82427E-04
5.000E&02	1.2520572836E-00	2.99423E-04
6.000E&02	1.2996256830E-00	3.23074E-04
7.000E&02	1.3462463967E-00	3.32063E-04
8.000E&02	1.3919194247E-00	3.25652E-04
9.000E&02	1.4366447668E-00	3.03692E-04
1.000E&03	1.4804224232E-00	2.67240E-04

From the results given in tables 1, 2, 3, 6, 7, and 8, the following significant results indicate that:

1. The least squares solution for the volume ratio at zero pressure, N, is not affected by errors of ±10% or ±20% in the fractional change of the effective area of the piston (at 25° C, P=0) with pressure. This was taken to mean that errors in b of as much as ±20% do not significantly influence the least squares value of the volume ratio at zero pressure.

2. The least squares solutions for B, assuming ±10% errors in b, differ from the second virial coefficient evaluated for b = -3.5×10^{-8} in^2/in^2 psi by about 1/17 the calculated uncertainty of this parameter; the corresponding differences for ±20% errors in b are about 9 times smaller than the uncertainty of B. This means, therefore, that errors of as much as ±20% in the value of the fractional change in the effective area of the piston (at 25° C, P=0) with pressure influences the least squares value of the second virial coefficient of the gas an insignificant amount.

3. The least squares solutions for the third virial coefficient, assuming errors of 0.8 b and 1.2 b, differ from C evaluated for 1.0 b by about 1/100 the calculated uncertainty of the third virial coefficient! The corresponding differences, assuming errors of 0.9 b and 1.1 b, are (1/200 S_C). This is interpreted to mean that errors in the value of b of as much as ±20% produce insignificant differences in the least squares solution of C, the third virial coefficient of the gas.

From the results given in tables 1, 2, 3, 6, 7, and 8, the following significant results indicate that:

1. The least squares solution for the volume ratio at zero pressure, N, is not affected by errors of ±10% or ±20% in the fractional change of the effective area of the piston (at 25° C, P=0) with pressure. This was taken to mean that errors in b of as much as ±20% do not significantly influence the least squares value of the volume ratio at zero pressure.

2. The least squares solutions for B, assuming ±10% errors in b, differ from the second virial coefficient evaluated for b = -2.5×10^{-6} in^2/in^2 psi by about 1\17 the calculated uncertainty of this parameter; the corresponding differences for ±20% errors in b are about 9 times smaller than the uncertainty of B. This means, therefore, that errors of as much as ±20% in the value of the fractional change in the effective area of the piston (at 25° C, P=0) with pressure influences the least squares value of the second virial coefficient of the gas an insignificant amount.

3. The least squares solutions for the third virial coefficient, assuming errors of 0.8 b and 1.2 b, differ from C evaluated for 1.0 b by about 1\100 the calculated uncertainty of the third virial coefficient. The corresponding differences, assuming errors of 0.9 b and 1.1 b, are (1\200 S_C). This is interpreted to mean that errors in the value of b of as much as ±20% produce insignificant differences in the least squares solution of C, the third virial coefficient of the gas.

4. The values of Z, assuming 0.8 b and 1.2 b, differ from Z evaluated for 1.0 b by about (1/5 S_Z) over the pressure range 1 to 700 atmospheres; the corresponding differences, assuming 0.9 b and 1.1 b, are almost an order of magnitude smaller than the uncertainty of the compressibility factor over this same pressure range. We conclude, therefore, that errors as great as 0.8 b and 1.2 b produce differences in Z which are no greater than 1/5 the uncertainty with which we know these compressibility factors over the pressure range of this experiment.

We also note that the independently determined value of the fractional change in the effective area of the piston (at 25° C, P=0) with pressure, b, has no significant influence on the precision of the PVT data or on N. This means, therefore, that <u>any</u> error in the determination of b should not affect the internal precision of compressibility measurements on the gas or the value of the zero pressure volume ratio of the Burnett apparatus. We found this to be true in the analysis of these data.

THE EFFECT AN ERROR OF IGNORING THE CHANGE IN THE VOLUME RATIO WITH PRESSURE PRODUCES IN Z, B, C, AND N

The final test applied to the experimental compressibility measurements of table 1 was to determine the effect an error of ignoring the pressure distortion of the bombs produces in the compressibility factor, the virial coefficients, and the zero pressure volume ratio and then to decide whether this assumption of $\alpha = \beta = 0$ differs significantly from the results previously calculated using the present values for these

pressure distortion coefficients (i.e., α = 1.6678 x 10^{-6} atm^{-1}, β = 1.6671 x 10^{-6} atm^{-1}).

Equation (1) was applied to the data of table 1, where Z_r is expressible by equation (2), to give the results of table 9 for α = β = 0. The values given in table 9 have the same meaning as those of table 2. From the results of table 9 and equation (2), the compressibility factors of table 10 were calculated. The deviations, S_Z, given in this table are standard deviations as determined by the method previously given in (8).

The results of tables 1, 2, 3, 9, and 10 indicate the following:

1. The least squares solution for N, assuming α = β = 0, differs from that evaluated for α = 1.6678 x 10^{-6} atm^{-1} and β = 1.6671 x 10^{-6} atm^{-1} by (1/100 S_N). This was interpreted to mean that ignoring the pressure distortion coefficients of the bombs does not produce a statistically significant difference in the least squares solution for the zero pressure volume ratio.

2. The solution for B, assuming α = β = 0, differs from that previously calculated using the present values for these pressure distortion coefficients by more than one would expect from the calculated uncertainties. This suggests, therefore, that ignoring the change in the volume ratio with pressure could be significant insofar as the second virial coefficient of the gas is concerned.

3. The solution for C, assuming α = β = 0, differs from that evaluated using the present values for these pressure distortion coefficients by no more than one would expect; that is, the difference is less

TABLE 9.-Results of the analysis of table 1, assuming the volume ratio to be independent of the pressure ($\alpha = 0 = \beta$)

r	P,OBS.,ATM.	P,CAL.,ATM.	P,OBS.-P,CAL.	$\frac{\text{P,OBS.-P,CAL.}}{\text{P,OBS.}}$
0	7.0128236E&02	7.0128236E&02	0.00000E-99	0.00000E-99
1	3.0170799E&02	3.0170849E&02	-5.01023E-04	-1.66062E-06
2	1.4061376E&02	1.4061111E&02	2.65149E-03	1.88565E-05
3	6.8033559E&01	6.8037141E&01	-3.58199E-03	-5.26504E-05
4	3.3517320E&01	3.3518817E&01	-1.49675E-03	-4.46560E-05
5	1.6660572E&01	1.6659325E&01	1.24671E-03	7.48301E-05
6	8.3186011E-00	8.3161219E-00	2.47917E-03	2.98027E-04
7	4.1639855E-00	4.1603349E-00	3.65058E-03	8.76703E-04

SUM OF WEIGHTED SQUARES OF THE RESIDUALS 4.33797E-05

CONSTANTS AND STANDARD ERRORS

N	1.994561338E-00	SN	1.30470E-04
B	5.259993502E-04	SB	8.87300E-07
C	-4.816958247E-08	SC	5.98977E-10

VARIANCES AND COVARIANCES

S2N	1.70224E-08
S2B	7.87302E-13
S2C	3.58774E-19
S2BC	-5.26578E-16
S2BN	-1.11476E-10
S2CN	7.18860E-14

TABLE 10.-Compressibility factors for helium at 0° C evaluated from the data of table 9 and equation (2)

PRESSURE, ATM.	Z	SZ
1.000E-00	1.0005259511E-00	1.06059E-06
2.000E-00	1.0010518060E-00	2.05352E-06
5.000E-00	1.0026287925E-00	4.90978E-06
1.000E&01	1.0052551765E-00	9.47836E-06
2.500E&01	1.0131198777E-00	2.25423E-05
5.000E&01	1.0261795435E-00	4.32272E-05
7.500E&01	1.0391789973E-00	6.30473E-05
1.000E&02	1.0521182391E-00	8.21807E-05
1.250E&02	1.0649972690E-00	1.00692E-04
1.500E&02	1.0778160869E-00	1.18607E-04
2.000E&02	1.1032730867E-00	1.52651E-04
2.500E&02	1.1284892386E-00	1.84249E-04
3.000E&02	1.1534645426E-00	2.13264E-04
3.500E&02	1.1781989987E-00	2.39535E-04
4.000E&02	1.2026926068E-00	2.62891E-04
4.500E&02	1.2269453671E-00	2.83158E-04
5.000E&02	1.2509572794E-00	3.00172E-04
6.000E&02	1.2982585604E-00	3.23823E-04
7.000E&02	1.3445964497E-00	3.32769E-04
8.000E&02	1.3899709474E-00	3.26277E-04
9.000E&02	1.4343820534E-00	3.04207E-04
1.000E&03	1.4778297677E-00	2.67628E-04

than the uncertainty with which we know this difference. We conclude, therefore, that ignoring the pressure distortion of N has an insignificant effect on the least squares value of C.

4. The compressibility factors of the gas calculated for zero distortion of the volume ratio with pressure differ from those evaluated using $\alpha = 1.6678 \times 10^{-6}$ atm^{-1}, $\beta = 1.6671 \times 10^{-6}$ atm^{-1} by more than is to be expected from the calculated uncertainties. This means, therefore, that the effect of ignoring the pressure distortion coefficients of the bombs has a statistically significant effect on the values of Z which amounts to more than three times the expected difference at 700 atmospheres; about twice the expected difference at 300 atmospheres, and about 1.4 times the expected difference at 50 atmospheres.

than the uncertainty with which we know this difference. We conclude, therefore, that ignoring the pressure distortion of N has an insignificant effect on the least squares value of C.

8. The compressibility factors of the gas calculated for zero distortion of the volume ratio with pressure differ from those evaluated using $\alpha = 1.6678 \times 10^{-6}$ atm^{-1}, $\beta = 1.6671 \times 10^{-9}$ atm^{-2} by more than is to be expected from the calculated uncertainties. This means, therefore, that the effect of ignoring the pressure distortion coefficients of the bombs has a statistically significant effect on the values of Z which amounts to more than three times the expected difference at 700 atmospheres; about twice the expected difference at 300 atmospheres, and about 1.4 times the expected difference at 30 atmospheres.

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